CORRELATION AND ESTIMATION METHODS FOR LIQUID THERMAL CONDUCTIVITY OF PROPANE SERIES REFRIGERANTS [1]

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[1] Paper presented at Thirteenth Symposium on Thermophysical Properties, June 25-30, 2000, Boulder, Colorado, U.S.A.

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ABSTRACT

The number of organic compounds used in industrial processes, energy production and applied research is constantly increasing. Between all new alternative refrigerants are checked both as pure fluids and as components of mixtures. The aim is to reach the optimum balance between efficiency and low, possibly null, ODP. Although some Propane series refrigerants have always been investigated, checked and utilised as refrigerants, the attention of refrigeration industry seems recently increased, especially for what concerns their use as components of mixtures. We present an extension of a previously developed predictive method to a new family of organic compounds, namely the Propane Family refrigerants. A simple equation relates the liquid thermal conductivity to the reduced temperature. It is effective in the range from the normal freezing point nearly to the critical point, though it does not take into account critical enhancement. Parameters and constants can be evaluated from easy available physical properties.

KEY WORDS: prediction method, thermal conductivity, refrigerants, Propane series.

INTRODUCTION

The number of organic compounds used in industrial processes, energy production and applied research is constantly increasing. Between all new alternative refrigerants are checked both as pure fluids and as components of mixtures. The aim is to reach the optimum balance between efficiency and low, possibly null, ODP. Although some Propane series refrigerants have always been investigated, checked and utilised as refrigerants, the attention of refrigeration industry seems recently increased, especially for what concerns their use as components of mixtures. Today, new procedures have been introduced to shorten the time required for tests and to reduce their cost. Computer modelling techniques and fast prototyping principles are the most important achievements in the field. Unfortunately they both require an "a priori" knowledge of all the properties introduced inside mathematical models describing the processes to be simulated. Between all, thermal conductivity is one of the most important properties.

The accuracy of prediction formulas has always been the most important feature of such tools. The quest for precision has often led to hyper-specialised formulas whose parameters had to be properly evaluated for each compound. The related prediction methods can be regarded as powerful tools but their application is limited to those substances for which the value of parameters has been correctly assessed. On the other hand, this often means that at least few measurements have to be performed.

Our approach to the prediction of transport properties has always been somewhat different. The original estimation methods, from which the equations we present in this paper have been derived, were originally conceived to evaluate transport properties of almost all the organic compounds in their saturated liquid state [1]. They required the value of a single experimental datum and their power mainly derived from their ability to cover almost all the families of organic compounds.

Having subsequently developed fully predictive equations we have applied them to a wide range of organic compounds and their mixtures. In particular we have proposed

new versions of the formulas to cover both Methane and Ethane series refrigerants. In this papere we present an extension of the previously developed predictive method to a new family of organic compounds, namely the Propane family refrigerants. A simple equation relates the liquid thermal conductivity to the reduced temperature. It is effective in the range from the normal freezing point nearly to the critical point, though it does not take into account critical enhancement. Parameters were extracted from easy available physical properties and evaluated for each family.

THE PREDICTION METHOD

The prediction method here applied to Propane Family refrigerants comes from the earlier work of Latini. His first approach to the evaluation of thermal conductivity of organic liquids led to a new form of Viswanath equation [2] modified for what concerned the "Packing Factor". Thus, the first form of the prediction method was proposed in 1981 [1] and was tested against a huge number of organic compounds grouped in families. To apply the method at least an experimental datum was required for each compound. At that point the prediction method still had a strong connection with physical models from which Viswanath derived his equation but was not a prediction method since it required experimental data.

In a second phase the equations were modified to avoid the introduction of experimental data thus showing full predictive capabilities [3] [4]. The later formulas have been specialised to evaluate transport properties of refrigerants, refrigerant mixtures, normal Alkanes and aromatic compounds. The main equation always assumed the same form but the parameters, a single one for the formula related to thermal conductivity, had to be evaluated from physical properties of compounds by means of specialised equations. In fact, such parameters strongly depended on the molecular structure of compounds thus justifying the necessity to apply each formula to the compounds belonging to the same family.

To apply the prediction method to Azeotropic and near-Azeotropic mixtures of refrigerants [6] we studied the behaviour of the refrigerants belonging to Methane series and

Ethane series. We found that a single formula could be applied to both families with an apparently acceptable increase in errors [6]. The prediction method we propose for the liquid thermal conductivity of Propane series refrigerants is an extension of such equation:

$$l = B \cdot \left(1 - \frac{3}{4} T_r\right) \qquad (1)$$

where l is the thermal conductivity [W/mK·10^3], T_r is the reduced temperature T/T_C and the constant B is linked with some thermophysical properties.

The latter and simpler formula to evaluate the constant B for Methane series and Ethane series refrigerants, was:

$$B = 0.85 \cdot T_c^{1/3} \cdot M^{-3/4} \qquad (2)$$

where M is the molecular mass and T_C is the critical point temperature [6]. It must be stressed that equation 2 was conceived to have a single formula applicable to both Ethane series and Methane series refrigerants and their mixtures. The use of other thermophysical properties was intentionally avoided since we found them not easily available in literature. The new equation was able to evaluate liquid thermal conductivity of all the refrigerants with errors still acceptable being typical mean deviations, with respect to experimental data, within 5% as shown in Table 1 where

AAD(%) = [Σabs($\lambda_{calc}/\lambda_{exp}$-1)]/n·100

and

MAD(%) = max of [abs($\lambda_{calc}/\lambda_{exp}$-1)]·100,

being λ_{exp} and λ_{calc} respectively the experimental and the estimated liquid thermal conductivity values and n the number of experimental points.

APPLICATION TO PROPANE SERIES REFRIGERANTS

Data about Propane series refrigerants are not easily available in literature. Vargaftik [7] collected data only about R214, R215, and R218. Moreover for R214 we had to evaluate

normal boiling point temperature and critical point temperature by means of Fedor and Joback estimation methods [8].

Due to the lack of experimental data we stated to check the prediction method against data evaluated by means of REFPROP 6 [9]. At this point one can object that we are going to validate a prediction method against predicted values. However we can point out that the original method has been validated against a huge number of experimental data related to Methane series and Ethane series refrigerants and we are now checking it against the Propane series refrigerants. Moreover, the results discussed in next chapter show that deviations against experimental data are of the same order of deviations against REFPROP data.

We firstly checked the equation 1 with the parameter *B* evaluated by means of equation 2. We found that errors were acceptable, as shown in Table 2, but a small increase of B would have led to a better agreement with experimental data. Thus we can propose a new form of equation 2 as:

$$B = 0.92 \cdot T_c^{1/3} \cdot M^{-3/4} \qquad (3)$$

were the variables have the same meaning of equation 2.

The parameter B is intended to be calculated by means of equation 3 when the equation 1 is used to evaluate the liquid thermal conductivity of Propane series refrigerants. The equation 2 is applicable to Methane, Ethane, and Propane series refrigerants and to their mixtures according to the rules stated in [6].

It must be stressed that our prediction method is intended for engineering applications. It is suitable for the evaluation of liquid thermal conductivity of those compounds whose behaviour has not been modelled more accurately by means of precise prediction method or software –e.g. REFPROP itself. However, the simplicity of the formulas and the minimal amount of input required make it a perfect tool for a broad range investigation about new refrigerants and new refrigerant mixtures.

RESULTS

Overall results are shown in Table 2 and Table 3. Table 2 and Figure 1 show deviations between predicted thermal conductivity and experimental data related to equation 1 with *B* parameter evaluated by means of equation 2. Deviations are of the same order of those achieved for Methane and Ethane series refrigerants as in Table 1. This means that the prediction method is applicable to Propane series refrigerants. It also means that the prediction method should be applicable to Azeotropic and near-Azeotropic mixtures of refrigerants containing any compound belonging to Methane, Ethane, and Propane series. Mean deviations range from few percentage units to a ten percent while maximum deviations are usually around 10%. Worst results are related to R214, R216, and R218, the only compounds we have experimental data about. The precision claimed for such data are about 3% [7] so we must take into account an apparent weakness of the formula about such important cases. However R214, R216, and R218 have the highest molecular mass and structure. As we could expect, our equations, originally specialised for Methane and Ethane series refrigerants, having lighter molecular masses and structures, show their weakness when applied to compounds with higher molecular masses.

Table 3 and Figure 2 show deviations between predicted thermal conductivity and experimental data with *B* parameter evaluated by means of equation 3. The results are obviously better since the equation 3 was tuned for Propane family refrigerants. Thus we recommend the application of this latter formula to evaluate the liquid thermal conductivity of Propane series pure refrigerants.

CONCLUSIONS

A prediction method is proposed for thermal conductivity of Propane family refrigerants. It evaluates thermal conductivity in the liquid state along the saturation line as a function of the reduced temperature. It requires the knowledge of a monomial

parameter which is related to easily available physical constants characteristic of each substance: critical temperature and molecular weight. The numerical constants to be used in the monomial parameter are given for all the investigated compounds.

The method shows average absolute deviations which are generally less than 5%, with maximum absolute deviations usually less than 10% in the reduced temperature range 0.30 to 0.95, though it does not take into account critical enhancement. Hence it can be useful for engineering purposes.

The method is based on the extension of equations previously developed for Methane and Ethane series refrigerants. Thus we can expect that the method is applicable to their mixtures according to the rules stated in [6].

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Compound	Reference	M	T_b [K]	T_c [K]	B	AAD [%]	MAD [%]
R112	[10]	203.83	366.0	551.0	0.1221	12.51	13.54
R113	[7] [11]	187.38	320.7	487.5	0.1274	6.42	14.20
R114	[7] [11] [12]	170.92	276.8	418.8	0.1331	1.60	4.48
R115	[7] [11] [13]	154.47	235.2	353.2	0.1396	1.33	3.13
R116	[10]	138.01	194.9	293.0	0.1472	5.05	5.50
R123	[12] [14-18]	152.93	301.9	456.9	0.1468	3.45	5.00
R123a	[12]	152.93	301.2	461.1	0.1470	1.15	1.90
R124	[7] [11] [12] [15]	136.47	260.0	395.6	0.1561	2.54	4.86
R125	[12] [18] [20][21]	120.02	224.7	339.3	0.1675	2.71	16.04
R132b	[14]	134.94	320.0	493.2	0.1633	6.11	8.89
R133a	[14]	118.49	279.2	432.0	0.1761	6.08	8.06
R134a	[14][14-17][22-26]	102.03	247.1	374.3	0.1923	6.05	10.01
R141b	[19] [25]	116.95	304.9	477.3	0.1808	4.92	14.76
R142b	[19] [26]	100.49	263.4	409.6	0.1975	10.20	13.33
R152a	[15] [19] [28]	66.050	248.5	386.7	0.2679	8.80	15.73
R10	[7]	153.82	349.9	556.3	0.1510	13.15	15.02
R11	[7] [11] [12] [29]	137.37	296.9	471.2	0.1599	3.72	6.01
R12	[7] [11] [12] [29]	120.91	243.4	385.0	0.1701	3.77	10.08
R13	[7] [11]	104.46	191.7	302.0	0.1823	7.02	12.90
R13B1	[7] [11]	148.91	215.5	340.2	0.1426	2.46	6.28
R20	[7]	119.38	334.3	536.4	0.1815	9.53	12.63
R21	[7]	102.93	282.1	451.7	0.1971	1.37	5.00
R22	[7] [11-12] [28-29]	86.47	232.3	369.3	0.2173	1.39	5.96
R23	[7] [30]	70.01	191.0	299.1	0.2457	3.37	6.50
R30	[7]	84.93	313.0	510.0	0.2324	6.25	7.05
R31	[7]	68.48	263.9	430.0	0.2654	6.79	8.71
R32	[20] [22]	52.02	221.6	351.4	0.3154	12.12	13.87

Table 1: Investigated refrigerants of Methane and Ethane series (equilibrium properties are taken from [8] [31] [32]).

Compound	Reference	M	T_b [K]	T_c [K]	B	AAD [%]	MAD [%]
R214	[7]	253.8	352	557	0.109973	9.04	14.66
R216	[7]	220.9	308.9	453.2	0.113931	7.28	8.02
R218	[7]	188	236.6	345.1	0.117421	11.34	13.31
R227EA	[9]	170	257.5	376	0.130287	1.94	3.80
R236ea	[9]	152	279.3	412.4	0.146129	5.61	7.05
R236fa	[9]	152	271.7	398.1	0.14441	4.00	8.12
R245ca	[9]	134.1	298.3	447.6	0.16504	6.79	8.93
R245fa	[9]	134.1	288.1	427.2	0.162497	5.84	8.76

Table 2. Investigated refrigerants of Propane series:
B evaluated by means of equation 2.
Equilibrium properties are taken from [8] [9] [31].

Compound	Reference	M	T_b [K]	T_c [K]	B	AAD [%]	MAD [%]
R214	[7]	253.8	352	557	0.119029	5.88	9.80
R216	[7]	220.9	308.9	453.2	0.123314	0.47	0.70
R218	[7]	188	236.6	345.1	0.127091	7.29	10.50
R227EA	[9]	170	257.5	376	0.141017	5.10	6.30
R236ea	[9]	152	279.3	412.4	0.158164	2.16	2.96
R236fa	[9]	152	271.7	398.1	0.156302	3.96	5.71
R245ca	[9]	134.1	298.3	447.6	0.178631	1.29	2.34
R245fa	[9]	134.1	288.1	427.2	0.175879	2.09	3.46

Table 3. Investigated refrigerants of Propane series:
B evaluated by means of equation 3.
Equilibrium properties are taken from [8] [9] [31].

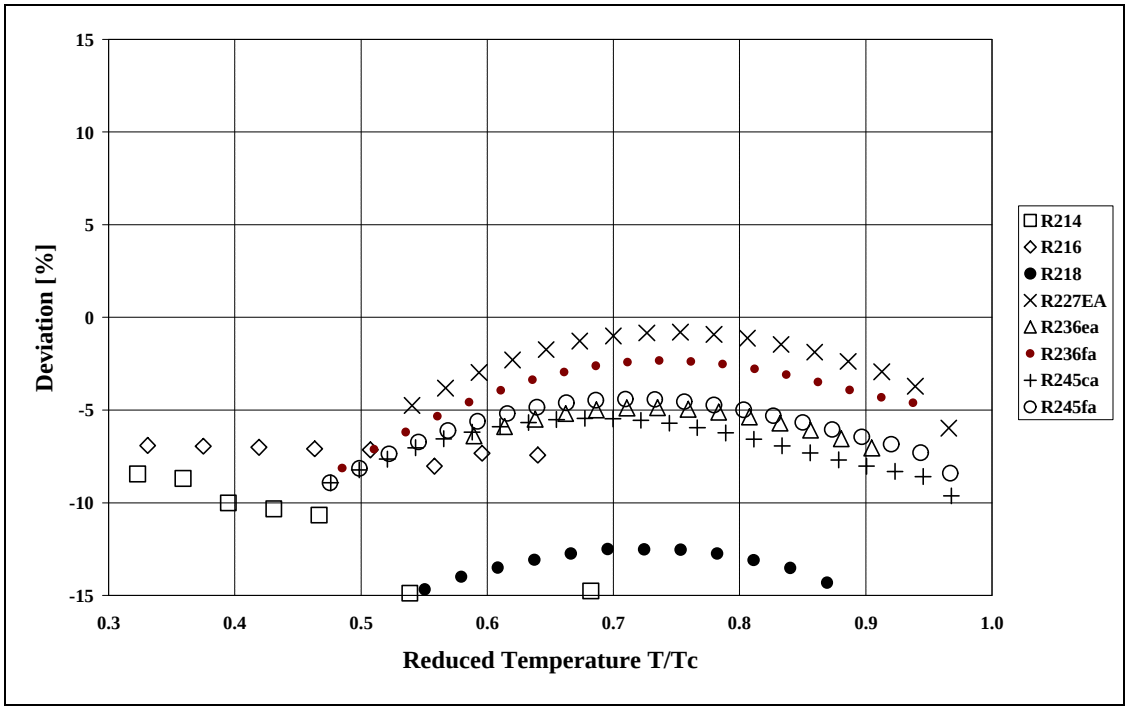

Fig. 1 – Deviations of predicted values against literature data.
Constant *B* evaluated by means of equation 2.

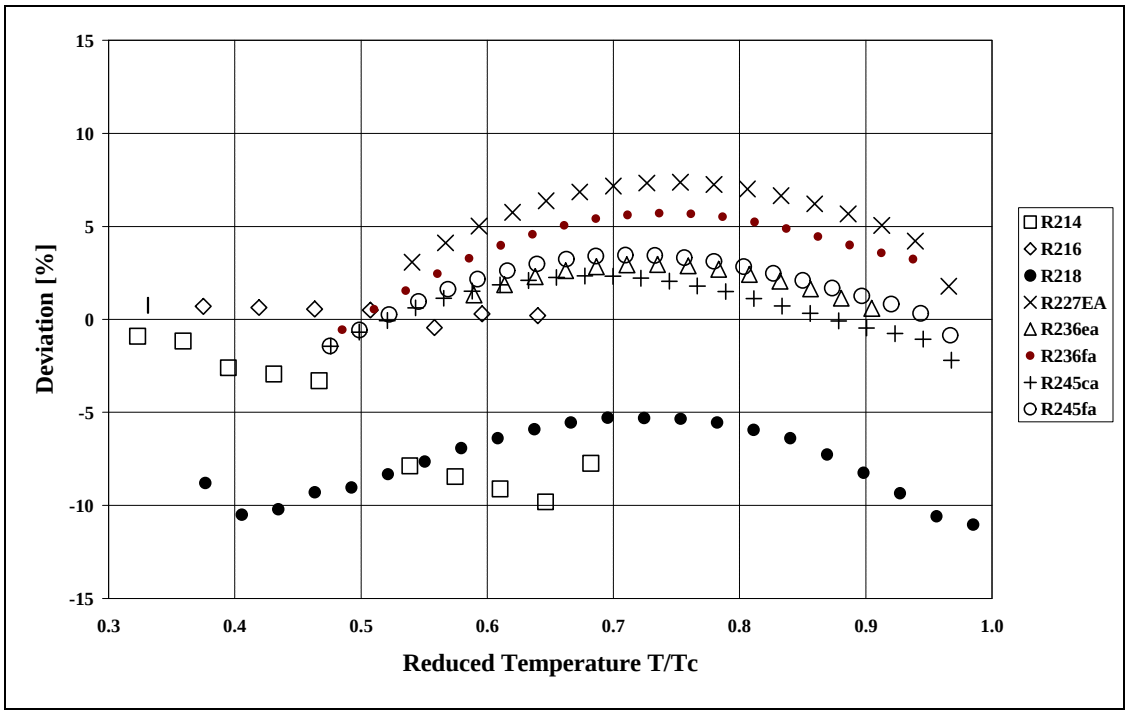

Fig. 2 – Deviations of predicted values against literature data.
Constant *B* evaluated by means of equation 3.